Polymerization of Phenylacetylenes. X. Polymerization of Diphenylacetylene by WCl_6- and $MoCl_5$-Based Catalysts*

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ABSTRACT: The polymerization of diphenylacetylene was investigated. The reaction was performed at 0—90°C in aromatic and halogenated hydrocarbons. The catalysts used are a mixture of WCl_6 and tetraphenyltin (W catalyst) and a mixture of $MoCl_5$, ethanol, and triethylaluminum (Mo catalyst). Polymerization smoothly proceeded by the W catalyst to give yellow insoluble poly-(diphenylacetylene) in high yield. The Mo catalyst also provided poly(diphenylacetylene), which is dark red and insoluble. The IR spectroscopy, differential thermal analysis, and X-ray diffraction showed that the former polymer was rich in *trans* structure and amorphous, and the latter rich in *cis* structure and crystalline. The electric conductivity and paramagnetic property of the polymer are also described.

KEY WORDS Coordination Polymerization / Diphenylacetylene / Tungsten Hexachloride / Molybdenum Pentachloride / Polyene / Geometric Structure / Crystallinity / Electric Conductivity /

Unlike vinyl polymers, acetylenic polymers are characterized by their color, semiconductivity, paramagnetism, and geometric isomerism. Acetylenic monomers, however, do not form high polymers by conventional radical, cationic, or anionic polymerization.[1] Only a few transition-metal catalysts are known to polymerize acetylenes to give high polymers: for example, $Ti(OC_4H_9)_4$–$4(C_2H_5)_3Al$ for acetylene,[2] Fe (III) acetylacetonate–$3(iso$-$C_4H_9)_3Al$ for alkylacetylenes,[3] and WCl_6 and $MoCl_5$ for phenylacetylene.[4] It is anticipated that disubstituted acetylenes are generally less reactive than unsubstituted and monosubstituted acetylenes, owing to steric effects.

The polymerization of diphenylacetylene (DPA) has been attempted so far by thermal[5] and anionic[6] initiations. In the thermal polymerization, however, only an oligomer (DP < 7) has been obtained, even though high temperatures up to 300—400°C have been employed. The oligomer formed is soluble in benzene. More recently, another oligomer (DP < 10;

benzene-soluble) of DPA has been obtained in the anionic polymerization initiated by alkali metals in tetrahydrofuran at 50°C. The ratio of catalyst to monomer in this polymerization is as high as 0.25—1.0, and the oligomer yield is less than 35%. No coordination catalyst has been reported to be effective for the polymerization of DPA. Thus no high polymer of DPA has been obtained up to the present.

We have found that an equimolar mixture of WCl_6 and tetraphenyltin (Ph_4Sn) works as a very active catalyst for the polymerization of phenylacetylene to give a polymer possessing a high molecular weight of 15,000.[7] The $WCl_6 \cdot Ph_4Sn$ catalyst is also capable of polymerizing 1-phenylpropyne; the molecular weight of the poly(1-phenylpropyne) (*ca.* 6000) is the highest among the values reported so far.[8] Further, we have found that mixture of $MoCl_5$, ethanol (EtOH), and triethylaluminum (Et_3Al) (1 : 1 : 2) shows the highest activity among the $MoCl_5$-based catalysts we have studied for the polymerization of phenylacetylene.[9]

In the present work, we examined in the polymerization of DPA the catalytic activities of $WCl_6 \cdot Ph_4Sn$ and $MoCl_5 \cdot EtOH \cdot 2Et_3Al$, which are effective for

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the polymerization of phenylacetylene. Further, the structure and properties of the poly(diphenyl-acetylene) [poly(DPA)] formed were studied in detail.

EXPERIMENTAL

DPA was prepared according to the literature procedure.[10] Though the crude product has been purified only by recrystallization in the literature, we further sublimed the yellow product and obtained white crystals. Yield 61%, mp 63°C (lit., yield 66%, mp 61°C[10]). Hexaphenylbenzene [$C_6(C_6H_5)_6$] was purchased from Aldrich Chem., and was purified by recrystallization from benzene.

The $WCl_6 \cdot Ph_4Sn$ catalyst was prepared by mixing equimolar amounts of WCl_6 and Ph_4Sn in a solvent and then keeping the mixture for 15 min at 60°C. Polymerization by the $MoCl_5 \cdot EtOH \cdot 2Et_3Al$ catalyst was performed as follows: Equimolar amounts of $MoCl_5$ and ethanol were mixed in a solvent in advance. Polymerization was initiated by adding Et_3Al and then the $MoCl_5 \cdot EtOH$ solution to a monomer solution. The conversion was determined by measuring the monomer consumption by means of gas chromatography. The polymer produced was washed with a mixture of methanol and $1.0 N$ HCl (9 : 1 vol ratio) to remove the catalyst residue. The polymer yield was determined by gravimetry.

Poly(DPA) was analyzed in the same manner as poly(phenylacetylene) and poly(β-naphthyl-acetylene), as described in previous papers.[11,12]

RESULTS AND DISCUSSION

Reactivity of DPA and Polymer Yield

Figure 1 shows the time–conversion curves for the $WCl_6 \cdot Ph_4Sn$-catalyzed polymerization of phenyl-acetylene and its homologs. Compared with the polymerizations of phenylacetylene and β-naphthyl-acetylene, three times as much catalyst was used for the polymerizations of 1-phenylpropyne and DPA. It is obvious from Figure 1 that the reactivities lie in the following order: phenylacetylene $\simeq$ β-naphthyl-acetylene $\gg$ 1-phenylpropyne > DPA. Thus DPA is much less reactive than monosubstituted acetylenes, and yet it is expected that DPA will give a polymer under suitable reaction conditions (e.g., a longer reaction time).
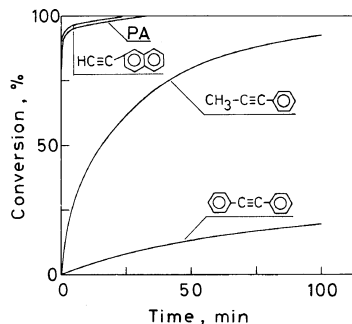
The polymerization of DPA hardly proceeded in

Figure 1. Polymerization of phenylacetylene and its homologs catalyzed by $WCl_6 \cdot Ph_4Sn$ in toluene at 30°C: $[WCl_6 \cdot Ph_4Sn]_0 = 10$ mmol dm^{-3} (phenylacetylene, β-naphthylacetylene), 30 mmol dm^{-3} (1-phenylpropyne, DPA); $[M]_0 = 1.0$ mol dm^{-3}.

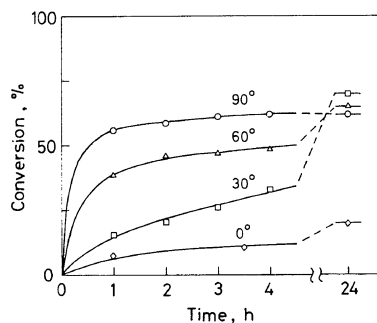**Figure 2.** Effect of temperature on the polymerization of DPA catalyzed by $WCl_6 \cdot Ph_4Sn$ in toluene: $[DPA]_0 = 1.0$ mol dm^{-3}, $[WCl_6 \cdot Ph_4Sn]_0 = 30$ mmol dm^{-3}.

the presence of WCl_6 unless Ph_4Sn was added as a reducing agent of WCl_6. The $MoCl_5 \cdot EtOH \cdot 2Et_3Al$ catalyst was less active for the polymerization of DPA than $WCl_6 \cdot Ph_4Sn$.

The effect of temperature was studied for the $WCl_6 \cdot Ph_4Sn$-catalyzed polymerization of DPA in toluene (Figure 2). The polymerization was performed for 24 h in the temperature range of 0—90°C. The initial polymerization rate increased with increasing temperature, whereas the conversion after 24 h was hardly affected by temperature above 30°C. This suggests that both propagation and termination reactions are accelerated with increasing temperature.

The influence of solvent on the polymerization of DPA at 60°C was examined. As seen from Figure 3, the polymerization occurred in aromatic hydrocarbons and in halogenated hydrocarbons. The polyme-
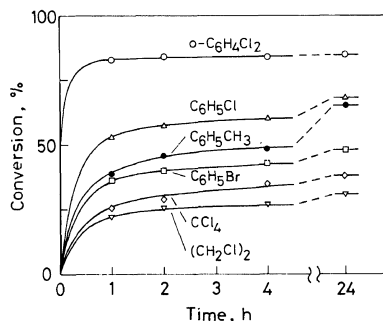
Figure 3. Effect of solvents on the polymerization of DPA catalyzed by $WCl_6 \cdot Ph_4Sn$ at 60°C: $[DPA]_0 = 1.0$ mol dm^{-3}, $[WCl_6 \cdot Ph_4Sn]_0 = 30$ mmol dm^{-3}.

rization did not achieve a stationary state in any solvent, but slowed down steeply with time. It is not evident how the nature of the solvent caused the differences in reaction rate and in asymptotic conversion.

Table I lists conversions and yields of a methanol-insoluble polymer after 24 h reaction in the above-mentioned polymerizations. The polymer yields were in a range of 20—60% in the polymerizations catalyzed by $WCl_6 \cdot Ph_4Sn$. The ratios of polymer yield to conversion were 0.3—0.85, which indicates that a methanol-soluble oligomer is more or less formed as a by-product. One result for the polymerization by $MoCl_5 \cdot EtOH \cdot 2Et_3Al$ is also involved in Table I. The conversion for the polymerization with the Mo catalyst was 27%, but the yield of a methanol-insoluble polymer was only 3%.

As mentioned in the Introduction, only soluble oligomers could be obtained in the earlier studies, although rather drastic conditions were employed. In contrast, the results described above shows that by use of $WCl_6 \cdot Ph_4Sn$ as a catalyst, the polymerization of DPA smoothly proceeded under mild conditions to give poly(DPA) in high yield.

Structure of Poly(DPA)

The values of elemental analysis for the polymer formed agreed well with the theoretical values (*e.g.*, poly(DPA) obtained by $WCl_6 \cdot Ph_4Sn$ in toluene. Calcd. for $C_{14}H_{10}$: C, 94.3%; H, 5.7% Found: C, 94.7%; H, 5.3%.).

Though the molecular weight could not be measured owing to polymer insolubility, the poly(DPA)s produced seem to have appreciably high molecular weights judging from their color, insolubility, and behaviors based on geometric structures which will be described later.

Figure 4 shows the IR spectra of two types of poly(DPA)s formed at 60°C in toluene, along with the spectra of hexaphenylbenzene and DPA. A large absorption is seen at $750 \, cm^{-1}$ in DPA; this absorption is fairly small in poly(DPA) obtained with $WCl_6 \cdot Ph_4Sn$ [denoted as poly(DPA)–W] and it can hardly be found in poly(DPA) formed with the Mo catalyst [denoted as poly(DPA)–Mo]. The spectra of poly(DPA)s differ from that of DPA in a region of $600—500 \, cm^{-1}$ as well. It is noticed that the spectrum of poly(DPA)–Mo resembles that of hexaphenylbenzene, which is the cyclic trimer of DPA.

Table I. Polymerization of DPA[a]

Catalyst	Solvent	Temp °C	Conversion %	Polymer Yield/%	Yield Conversion
$WCl_6 \cdot Ph_4Sn$	$C_6H_5CH_3$	90	62	47	0.76
''	''	60	65	49	0.75
''	''	30	70	57	0.81
''	''	0	20	17	0'85
''	C_6H_5Cl	60	68	35	0.51
''	C_6H_5Br	60	48	41	0.85
''	$o–C_6H_6Cl_2$	60	85	27	0.32
''	CCl_4	60	37	22	0.59
''	$(CH_2Cl)_2$	60	30	20	0.67
$MoCl_5 \cdot EtOH$ $2Et_3Al$	$C_6H_5CH_3$	60	27	3	0.11

[a] $[DPA]_0 = 1.0$ mol dm^{-3}; $[Cat]_0 = 30$ mmol dm^{-3}, 24 h.

Figure 4. IR spectra of poly(DPA) and related compounds.

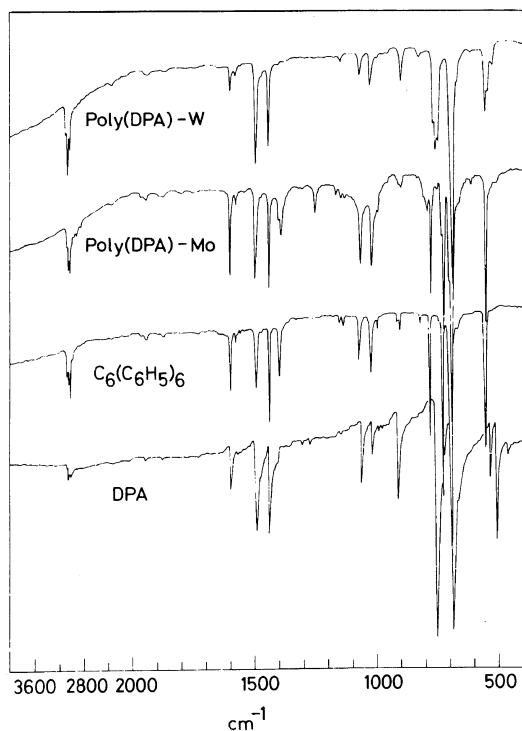**Figure 5.** DTA curves of poly(DPA) and related compounds.

Large differences are seen at 1600, 1400, 800—700, and 550 cm^{-1} between the IR spectra of poly(DPA)–W and poly(DPA)–Mo. Also in the cases of phenylacetylene[11] and β-naphthylacetylene,[12] the two types of polymers obtained with WCl$_6$ and MoCl$_5$ have shown different IR spectra; this has been explained in terms of geometric structure. Therefore, the differences between the IR spectra of the two poly(DPA)s are reasonably attributed to geometric structures of the main chain. The IR spectrum of poly(DPA)–W hardly depended on the temperature and solvent of polymerization.

The polymers were examined by differential thermal analysis with respect to their thermal properties and geometric structure. Only an exotherm which gradually occurs above 280°C is observed in poly(DPA)–W (Figure 5); this exotherm is explained in terms of hydrogen migration, scission of main chain, and so on. On the other hand, poly(DPA)–Mo exhibits a sharp exothermic peak at 280°C, besides the above exotherm. Such peaks have generally been observed in *cis*-rich acetylenic polymers and been
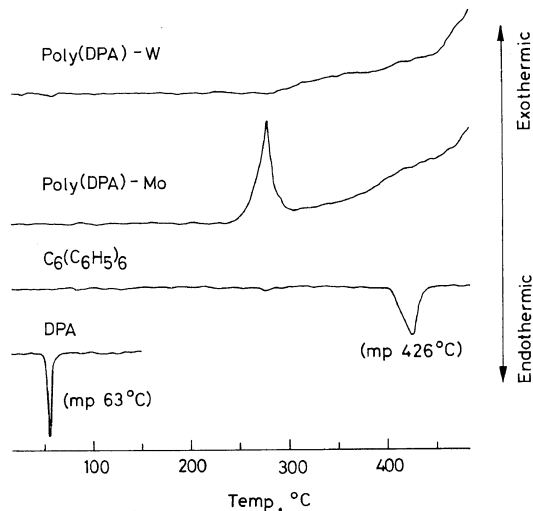
considered to be due to *cis*-to-*trans* isomerization.[13,14] Therefore the observed exothermic peak presents evidence that poly(DPA)–Mo is rich in *cis* structure, compared with poly(DPA)–W. Hexaphenylbenzene and DPA showed only endotherms at their melting points, 426°C and 63°C, respectively. Since these endotherms are not seen in the two polymers, it is concluded that neither HPB nor DPA exists in these polymers.

Figure 6 gives X-ray diffraction patterns for the powdery smaples of two types of poly(DPA)s and of hexaphenylbenzene. Poly(DPA)–W showed no crystalline pattern, while clear rings were observed in poly((DPA)–Mo. Spots seen in the pattern of poly(DPA)–Mo are due to hard polymer particles which could not be ground to a very fine powder. A tendency for *cis*-rich acetylenic polymers to be highly crystalline and insoluble has also been observed in poly(phenylacetylene)[15] and poly(β-napthylacetylene).[12] *Cis* polymers are assumed to take a helical conformation where substituents are directed toward the outside; this probably is the reason for the high crystallinity. The crystalline pattern of hexaphenylbenzene was obviously different from that of poly(DPA)–Mo.

The results of IR spectroscopy, differential thermal analysis, and X-ray diffraction of poly(DPA) lead to the following conclusion on polymer structure: Poly(DPA)–W is rich in *trans* structure and
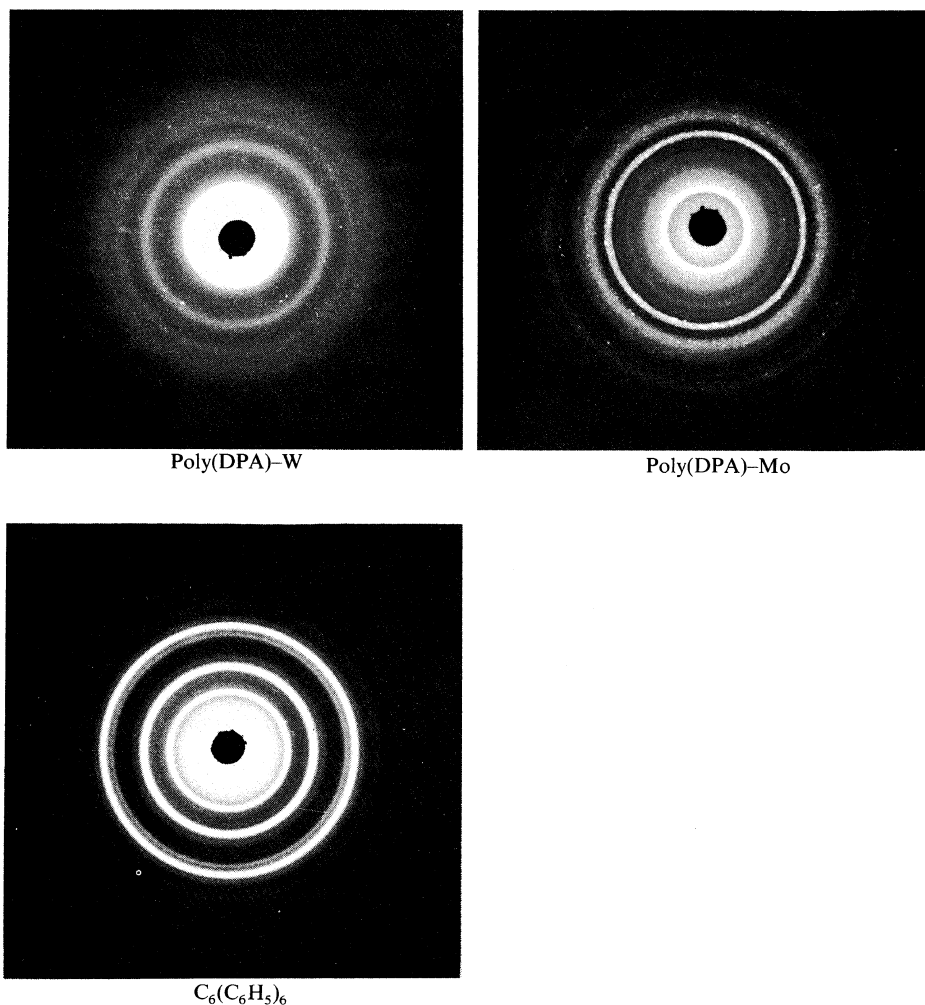
Poly(DPA)–W

Poly(DPA)–Mo

$C_6(C_6H_5)_6$

Figure 6. X-ray diffraction diagrams of poly(DPA) and HPB.

amorphous, while poly(DPA)–Mo is rich in *cis* structure and crystalline.

Properties of Poly(DPA)

Poly(DPA)–W was yellow irrespective of polymerization conditions, whereas poly(DPA)–Mo was dark red. This contrasts with the finding that poly(phenylacetylene) prepared with WCl_6 was dark brown, and that formed by $MoCl_5$ was yellow.[11] Hexaphenylbenzene is a white powder.

Both poly(DPA)–W and poly(DPA)–Mo were insoluble in any common solvents, although their geometric structures were significantly different from each other. This suggests that poly(DPA) is insoluble

irrespective of its geometric structure. On constructing the molecular models of *cis* and *trans* poly(DPA)s, one will notice that the polymer chains are so crowded with phenyl groups and rigid that it should not dissolve. Hexaphenylbenzene dissolves in common organic solvents, though it is not very soluble.

It has been known that polyacetylene is insoluble, regardless of its geometric structure. On the other hand, poly(phenylacetylene) is soluble in aromatic and halogenated hydrocarbons unless its *cis* content is very high.[11] Poly(1-phenylpropyne), which is a polymer of disubstituted acetylene, is also soluble.[7] Thus the solubility of acetylenic polymers depends

on the nature and number of substituents as well as the geometric structure of the main chain.

Poly(DPA)–W and poly(DPA)–Mo were infusible; they showed no softening points, but gradually decomposed at elevated temperatures. This is the same tendency as that seen for polyacetylene. On the other hand, poly(phenylacetylene) exhibits a softening point at around $220°C$.[11]

The electric and magnetic properties of poly-(DPA)–W are shown in Table II. The electric

Table II. Electric and magnetic properties of poly(DPA)[a]

Polymerization solvent	Polymerization temp/°C	σ	Unpaired spin/g^{-1}
		$S\,cm^{-1}$	
$C_6H_5CH_3$	90	2.4×10^{-15}	4.4×10^{18}
"	60	5.2×10^{-16}	3.6×10^{18}
"	30	9.2×10^{-17}	1.4×10^{18}
C_6H_5Cl	60	1.3×10^{-15}	3.9×10^{17}
C_6H_5Br	60	9.7×10^{-15}	8.7×10^{17}
$o\text{-}C_6H_4Cl_2$	60	7.1×10^{-14}	1.0×10^{18}

[a] Polymerized for 24 h, $[DPA]_0 = 1.0\ mol\,dm^{-3}$. $[WCl_6 \cdot Ph_4Sn]_0 = 30\ mmol\,dm^{-3}$.

conductivities of poly (DPA)–W were in the range of 10^{-17}—$10^{-14}\,S\,cm^{-1}$. These values are analogous to those of poly(phenylacetylene)[11] and poly(β-naphthylacetylene).[12] As the conductivity of polyacetylene is 10^{-9}—$10^{-5}\,S\,cm^{-1}$,[16] the introduction of one or two aryl groups as substituent results in a remarkable decrease in the conductivity. This suggests that aryl groups as substituents twist the main chain and reduce the conjugation.

The electron spin resonance spectrum of poly(DPA) showed a structureless single line, whose g value was 2.00185 G and whose peak-to-peak width was 4.8 G. The unpaired spin densities of poly(DPA)–W were 10^{17}—$10^{18}\ g^{-1}$ (see Table II). Consequently the spin densities of polyacetylene,[17] poly(phenylacetylene),[11] and poly(DPA) are all in the range of 10^{16}—$10^{18}\ g^{-1}$, which means that the presence of one or two phenyl groups as substituents does not affect spin density very much in acetylenic polymers.

To summarize polymer properties, the poly-(DPA)s obtained with WCl_6- and $MoCl_5$-based catalysts are colored, insoluble, infusible, and show electric conductivities and spin densities similar to those of poly(phenylacetylene).

REFERENCES

1. See, as a review, M. G. Chauser, Yu. M. Rodionov, V. M. Misin, and M. I. Cherkashin, *Uspekhi Khim.*, **45**, 695 (1976); *Russ. Chem. Rev.*, **45**, 348 (1976).
2. T. Itoh, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 11 (1974).
3. W. J. Trepka and R. J. Sonnenfeld, *J. Polym. Sci., A–1*, **8**, 2721 (1970).
4. T. Masuda, K. Hasegawa, and T. Higashimura, *Macromolecules*, **7**, 728 (1974).
5. P. P. Kisilitsa, M. I. Cherkashin, and A. A. Berlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1959 (1967).
6. V. M. Misin, P. P. Kisilitsa, N. I. Bolondayeva, and M. I. Cherkashin, *Vysokomol. Soedin., Ser. A*, **18**, 1726 (1976).
7. T. Masuda, K.-Q. Thieu, N. Sasaki, and T. Higashimura, *Macromolecules*, **9**, 661 (1976).
8. N. Sasaki, T. Masuda, and T. Higashimura, *Macromolecules*, **9**, 664 (1976).
9. H. Kawai, T. Ohtori, T. Masuda, and T. Higashimura, unpublished data.
10. "Organic Synthesis," Coll. Vol. III, E. C. Horning, Editor-in-Chief, John Wiley & Sons, Inc., New York, N.Y., 1955, p 350.
11. T. Masuda, N. Sasaki, and T. Higashimura, *Macromolecules*, **8**, 717 (1975).
12. T. Ohtori, T. Masuda, and T. Higashimura, *Polym. J.*, **11**, 805 (1979).
13. T. Itoh, H. Shirakawa, and S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1943 (1975).
14. C. I. Simionescu, S. Dumitrescu, V. Percec, and M. Grigoras, *Rev. Roum. Chim.*, **22**, 1105 (1977).
15. S. H. C. Chang, E. C. Mertzlufft, P. Ehrlich, and R. D. Allendoerfer, *Macromolecules*, **8**, 642 (1975), and the references therein.
16. H. Shirakawa, T. Itoh, and S. Ikeda, *Makromol. Chem.*, **179**, 1565 (1978).
17. W. H. Watson, Jr., W. C. McMordie, Jr., and L. G. Lands, *J. Polym. Sci.*, **55**, 137 (1961).